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⑤④ **Alumina coated sintered body.**

⑤⑦ According to the invention there is now provided a sintered hard material body at least partly coated with at least one 0.5-20  $\mu\text{m}$  wear resistant ceramic oxide coating being <80% thicker in the edges than on the flat surfaces. The oxide coating exhibits a grain size ( $\phi$ ) in  $\mu\text{m}$  for which :

$$\phi \leq kx + 1$$

where x is coating thickness in  $\mu\text{m}$  on at least 80% of the flat surfaces of the body,

k = 0.5, preferably 0.3 and

1 = 2  $\mu\text{m}$  for  $4 \leq x < 20$  and 1=0 for  $0.5 < x < 4$ .

The oxide coating is achieved by using a deposition process in which the body is in contact with a gas containing one or more halides of a metal or metals and a hydrolysing and/or oxidizing agent forming the metal oxides and with an additional reactant (dopant) of sulphur, phosphorus, selenium, tellurium, arsenic, antimony and/or bismuth and/or compounds thereof. The temperature during deposition is in the range of 800-1000°C, preferably 850-970°C, and the volume concentration of the additional reactant is 0.25-3, preferably 0.3-1 % of the total gas volume.

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the entire deposition period.

A lower deposition temperature also decreases the rate of potential surface oxidation leading to alpha nucleation.

Up to this date, there has not been reported any reliable method for successfully depositing hard, adherent, high-quality alumina coatings in the desired low-temperature region, e.g. below 1000°C and, in particular, below 950°C. When deposition of alumina is carried out by known methods below 950°C, only very thin, powdery deposits are obtained.

A low process temperature during the alumina deposition has been mentioned in previous patents but only in connection with very thin coatings and while utilizing very different CVD processes e.g. with Al-metallo-organic compounds as reactants, or e.g. with H<sub>2</sub>O as the oxygen source e.g. Lux US 3,836,392. This type of processes is not being used for commercial coating of cemented carbides.

According to the invention there is now provided a method for depositing and producing high-quality, well-adherent thin (0.5-4 µm), or preferably thick (4-20 µm) ceramic oxide coatings with a high growth rate. The coatings have an evenly distributed layer thickness around the entire coated body and a smooth coating surface and fine grain size. The deposition process temperature can range from 800 to 1000°C, preferably 850 to 970°C or most preferably from 900 to 950°C. During the deposition process said body is in contact with a gas containing one or more halides of a metal or metals and a hydrolysing and/or oxidizing agent forming the metal oxides and with an additional reactant (dopant) with a concentration of 0.25-3 %, preferably 0.3-1 % and most preferably 0.4-0.8 % of the total gas volume being used during the CVD process. The additional reactant is preferably sulphur and/or phosphorus or a compound of these but can equally well be selenium, tellurium, arsenic, antimony or bismuth or compounds and/or mixtures of all these reactants. Examples of such reactants or dopants are hydrogen sulphide (H<sub>2</sub>S), phosphorus chloride (PCl<sub>3</sub>), carbon oxysulphide (COS) and phosphine (PH<sub>3</sub>). Preferably hydrogen sulphide is used.

Hence, the use of higher concentration of the additional dopant (reactant) in combination with lower process temperature than were actually employed in Smith 4,619,866 a smooth, high-quality, well-adherent ceramic oxide coating can be successfully grown. Furthermore, the grain-size of the coating can be controlled by carefully varying the dopant concentration and/or the temperature during the nucleation step and during the subsequent growth period.

Preferably, the ceramic oxide is Al<sub>2</sub>O<sub>3</sub> and/or ZrO<sub>2</sub>. Most preferably the ceramic oxide is Al<sub>2</sub>O<sub>3</sub> consisting essentially, preferably of more than 85%, of the kappa phase or other metastable modification. The kappa-to-alpha ratio can be controlled in the same way as the grain size as indicated above.

If coatings less than 4 µm in thickness are produced according to the invention, still finer-grained coatings will result as compared to coatings produced by prior-art CVD-processes. The grain size Ø in µm, can be expressed as follows:

$$\text{Ø} \leq kx$$

where x is coating thickness in µm on at least 80% of the flat surfaces of the body and k = 0.5, preferably 0.3 and most preferably 0.15.

In the lower temperature region, 850-950°C, and with a fairly high volume concentration of dopant (0.5-2%) in the process gas, thick (4-20 µm), fine-grained, preferably < 2 µm, 100 % kappa Al<sub>2</sub>O<sub>3</sub> coatings can readily be grown. The grain size Ø in µm, can be expressed as follows:

$$\text{Ø} \leq kx + 2$$

where x is coating thickness in µm on at least 80% of the flat surfaces of the body and k = 0.5, preferably 0.3 and most preferably 0.15.

Within the fine-grained coating according to this invention, occasionally some larger grains can be present. In some cases these large grains may cover up to 10 % of the coated surface. The growth of these large grains may be caused by impurities or dust particles that occasionally are present in the CVD process gas. The larger grains may also originate from oxidized micro-spots on the underlying surface as was discussed previously.

In accordance with known technique a coating according to the invention can be used as a single coating or be deposited on e.g. TiC or TiCON intermediate layers. Further coatings can be deposited on top of the ceramic coating, e.g. TiN and the oxide coating of the present invention can be used within a multicoating structure.

Preferably, an innermost layer with a thickness of 0.5-10 µm and comprising at least one member selected from the group consisting of the carbides, nitrides, carbonitrides and oxycarbonitrides of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W or B is used.

The products produced according to the invention, include inserts for cutting tools made of cemented carbides, cermets or ceramics, furthermore end mills, drills, reamers, broaches and general wear parts made of steel, high speed steel, cemented carbide, cermets and ceramics.

When fine-grained Al<sub>2</sub>O<sub>3</sub> coated cemented carbide cutting tools according to the invention are used in metal machining, several important improvements have been observed:

coatings, were tested. It could readily be seen that the insert according to the invention, No 4, was much less worn than the prior art insert, No 3.

## Example 2

(Run No. 1) Commercial cemented carbide inserts of composition 5.5% Co, 2.6% TiC, 6.2% TaC/NbC and balance WC were coated in a reactor similar to the one described in example 1. However, this reactor could be loaded with a significantly larger amount of inserts (up to 16 000 inserts).

The inserts were sequently coated with TiC (1  $\mu\text{m}$ ), TiCN (4  $\mu\text{m}$ ) and  $\text{Al}_2\text{O}_3$  (6  $\mu\text{m}$ ). For the TiC process, a gas composition of 4%  $\text{TiCl}_4$  and 6%  $\text{CH}_4$  was used at 1030°C and for the TiCN process, a gas composition of 4%  $\text{TiCl}_4$ , 6%  $\text{CH}_4$  and 15%  $\text{N}_2$  at 1030°C was used. Prior to the  $\text{Al}_2\text{O}_3$  deposition start, the process temperature was reduced to 960°C.  $\text{Al}_2\text{O}_3$  was then deposited for 8 hours with a reaction gas containing 5%  $\text{CO}_2$ , 3%  $\text{AlCl}_3$  and 0.4%  $\text{H}_2\text{S}$ .

(Run No. 2) The TiC and TiCN depositions were identical to those in run No 1. Prior to the  $\text{Al}_2\text{O}_3$  deposition start, the temperature was increased to 1040°C and  $\text{Al}_2\text{O}_3$  was deposited for 5.5 hours with a gas composition of 5%  $\text{CO}_2$ , 3%  $\text{AlCl}_3$  and 0.25%  $\text{H}_2\text{S}$ .

The metallurgical investigation showed that inserts from Run No. 1 exhibit a smooth, fine-grained  $\text{Al}_2\text{O}_3$  coating of 100 % kappa phase (according to XRD), whereas inserts from Run No. 2 had a mixed grain structure, both large grains and smaller grains. XRD shows 100 % alpha phase.

Tool inserts from run No 1 and No 2 were compared in a cutting operation machining ball bearing rings in which severe chip hammering of the tool surface occurs. The following results were obtained:

Insert from run No.	Produced pcs of ball bearing rings	Tool failure criterium
1	66	worn out
2	5	edge breakage

It is presumably the inherent cracks and porosity in the alpha  $\text{Al}_2\text{O}_3$  coating obtained in run No 2 that are responsible for the early breakage of the cutting edge and the reduced tool life observed in the test.

## Claims

1. Sintered hard material body at least partly coated with at least one 0.5-20  $\mu\text{m}$  wear resistant ceramic oxide coating being <80% thicker in the edges than on the flat surfaces characterized in that said oxide coating exhibits a grain size ( $\phi$ ) in  $\mu\text{m}$  for which:

$$\phi \leq kx + 1$$

where x is coating thickness in  $\mu\text{m}$  on at least 80% of the flat surfaces of the body,

k = 0.5, preferably 0.3 and

1 = 2  $\mu\text{m}$  for  $4 \leq x < 20$  and 1=0 for  $0.5 < x < 4$ .

2. Compound body according to claim 1 characterized in having an innermost layer with a thickness of 0.5-10  $\mu\text{m}$  and comprising at least one member selected from the group consisting of the carbides, nitrides, carbonitrides and oxycarbonitrides of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W or B.
3. Compound body according to claim 1 or 2 characterized in that the oxide coating is  $\text{Al}_2\text{O}_3$  and/or  $\text{ZrO}_2$ .
4. Compound body according to claim 3 characterized in an  $\text{Al}_2\text{O}_3$ -coating consisting of at least 85% kappa  $\text{Al}_2\text{O}_3$  or other metastable polymorphs of alumina.
5. Compound body according to any of the claims 1 - 4 characterized in that the ceramic oxide coating or coatings have a grain size which is less than 2  $\mu\text{m}$ .
6. Compound body according to any of the preceding claims characterized in that the ceramic oxide coating



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# EUROPEAN SEARCH REPORT

Application Number

EP 92 85 0155

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	EP-A-0 045 291 (SANDVIK AKTIEBOLAG) * page 15, line 15 - line 20; claims 1-3 *	1-9	C23C16/40 B23B7/14 C04B41/50
Y,D A	EP-A-0 403 461 (SANDVIK AKTIEBOLAG) * page 1, line 45 - line 48; example 1 *	1-6 7-9	
Y	JOURNAL OF THE ELECTROCHEMICAL SOCIETY vol. 125, no. 6, 1 June 1978, pages 902 - 907 V.J.SILVESTRI ET AL. 'PROPERTIES OF AL2O3 FILMS DEPOSITED FROM THE ALCL3, CO2, AND H2 SYSTEM' * page 903, left column, line 7 - line 36 *	7-9	
A	* page 905, right column, line 12 - line 22; figure 5 *	1-6	
A	EP-A-0 408 535 (SECO TOOLS AB.) * column 2, line 13 - line 39; claims 1,2,8 *	1-9	TECHNICAL FIELDS SEARCHED (Int. Cl.5)  C23C
A,D	EP-A-0 084 525 (SANTRADE LTD.) * page 5, line 3 - line 17; claims 1-3 *	1-9	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 06 OCTOBER 1992	Examiner EKHULT H.U.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document	

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